



Maximization of photocatalytic activity of $\text{Bi}_2\text{S}_3/\text{TiO}_2/\text{Au}$ ternary heterostructures by proper epitaxy formation and plasmonic sensitization

Sumana Paul¹, Sirshendu Ghosh^{1,2}, Dulal Barman, S.K. De*

Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata, 700032, India

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ABSTRACT

Ternary $\text{Bi}_2\text{S}_3/\text{TiO}_2/\text{Au}$ heterostructure has been successfully synthesized by decorating Au nanoparticles onto binary $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructure. Structural analysis suggests that the heterostructure consists of orthorhombic Bi_2S_3 , tetragonal anatase TiO_2 and face centered cubic Au. The appearance of extra Raman peak at 123 cm^{-1} and the modification of Raman peaks of Bi_2S_3 and TiO_2 phases indicates a significant molecular interaction during growth of TiO_2 nanocrystals (NCs) on the surface of Bi_2S_3 nanorods. Self assembly of nanorods triggered by oleic acid results in urchin like morphology of pure Bi_2S_3 . The $\{011\}$ facet of TiO_2 nanocrystals grow epitaxially on $\{013\}$ facet of Bi_2S_3 nanorods. Periodic arrangement of (111) plane of Au and (011) plane of Bi_2S_3 favors epitaxial growth in $\text{Bi}_2\text{S}_3/\text{TiO}_2/\text{Au}$ heterostructure. Unique design of the ternary heterostructure makes a preferable pathway for the photogenerated electrons by suppressing the electron-hole recombination. The observation of decreased electron spin resonance signal intensity based on spin label technique confirms the electron transfer from photoexcited heterostructure. Favorable energetic positions of conduction and valence band edges of semiconductors (Bi_2S_3 and TiO_2) and Fermi level of metal (Au) are the key factors to enhance the photocatalytic activity of ternary heterostructure. Plasmonic phenomenon of metal (Au) nanoparticles by changing their size and shape was also investigated to remove organic pollutants from waste water.

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1. Introduction

For cleaner and greener world, development of green photocatalyst is very important for alternative energy source like H_2 gas production by water splitting and degradation of hazardous organic dyes which are used daily for betterment of human life. In present situation of nanoscience research, nanoscale metal-semiconductor and semiconductor-semiconductor hybrid heterostructures with various morphology and tuneable size are most emerging candidates for solar energy conversion, photocatalysis and optoelectronic devices [1–4]. To be a potent candidate to show excellent photoactivity, efficient charge separation in semiconductor is very essential. Under the band gap excitation, electron-hole (e-h) pair (exciton pairs) is formed both in bulk and surface. But exciton pair formed in bulk is not useful, as the photo-

tocatalysis process is a surface phenomenon in semiconductors. Migration of exciton from bulk to surface site is often slow and they normally recombine in midway. So increase the surface area by lowering the dimension of semiconductor is one of the fruitful way to improve the efficiency of photocatalytic activity [5]. Among the green oxides, TiO_2 and ZnO are the most promising candidates for their high earth abundance [6,7]. TiO_2/ZnO allows the formation of an e-h pair only when irradiated by ultra-violet (UV) light of the whole solar light spectrum. But in terms of available energy, visible (43%) and infrared (52%) light constitute most of the solar emission with a very low amount of UV (4%) light [8]. This is the biggest problem for maximum solar photon utility of most commercialised TiO_2 based photocatalyst P25. Also the high recombination rate of photogenerated electron and hole in TiO_2 often leads to a low quantum yield and poor photocatalytic activity. Different efforts have been taken to overcome the limitation of titania, such as doping, decreasing the crystallite size and photosensitization of TiO_2 . The band gap can be decreased by doping but the process has some disadvantages: (i) introduction of impurity can strongly affect the life time of e-h pair and might act as recombination centre, (ii) doping also can decrease the corrosion resistance of the TiO_2 (especially when

* Corresponding author.

E-mail addresses: msskd@iacs.res.in, skdiacs@gmail.com (S.K. De).

¹ Authors contributed equally.

² Present address: Department of Chemistry, National Cheng Kung University, Tainan, Taiwan.

the dopant is transition metal ions). Although the attachment of organic dyes with TiO_2 is somehow fruitful [9,10] for photosensitization of TiO_2 but still face major problems in photocatalysis like poor stability of dye which can undergo oxidative degradation of dyes or fast back electron transfer.

Recent researches [11,12] established that combination of wide band gap photocatalyst with narrow band gap semiconductors like metal chalcogenides might be an effective way to harvest solar light on a broad scale which also prompts the charge separation and results in high photocatalytic activity like H_2 generation [13]. Metal sulfide- TiO_2 nanoheterostructures (NHS) including PbS-TiO_2 , $\text{WS}_2\text{-TiO}_2$, $\text{MoS}_2\text{-TiO}_2$, $\text{FeS}_2\text{-TiO}_2$ and CdS-TiO_2 exhibit high photocatalytic activity and photovoltaic performances [14–17,12]. Fang et al. has reported [18] high yield H_2 generation in $\text{Au@TiO}_2\text{-CdS}$ ternary NHS. Although CdS is a promising candidate for enhancing the photoactivity of TiO_2 but it faces toxicity problem of Cd . Bismuth sulfide (Bi_2S_3) can be a better substitution as it has an absorbance onset at $\sim 1.3\text{--}1.5\text{ eV}$ with high absorbance coefficient (10^4 cm^{-1}) [19]. Thus Bi_2S_3 is able to harvest visible light from the solar spectrum and a greener material too. Bi_2S_3 is an excellent photoconductive semiconductor and a promising candidate for electrochemical hydrogen storage, hydrogen sensing and biomolecule detection. But severe recombination of photogenerated e-h is a major problem which results in low quantum yield. Complete e-h separation can be done by attachment of metal or semiconductor NCs onto Bi_2S_3 surface having proper band alignment. As the conduction band (CB) energy level of Bi_2S_3 is 0.26 eV higher than TiO_2 , the photo generated electrons can be smoothly transferred from Bi_2S_3 to TiO_2 . Whereas valence band (VB) of TiO_2 is lower than that of Bi_2S_3 , so photogenerated hole can be transferred to Bi_2S_3 . So complete separation of e-h in both TiO_2 and Bi_2S_3 is possible and $\text{Bi}_2\text{S}_3/\text{TiO}_2$ NHS results in a type-II band alignment [20,21]. Previous reported $\text{Bi}_2\text{S}_3/\text{TiO}_2$ reveals visible light induced hydrogen evolution and photocatalytic activity but not such a higher extent than pure Bi_2S_3 or TiO_2 [22]. Most of these reports demonstrated the uncontrolled deposition of Bi_2S_3 onto TiO_2 surface without any proper epitaxy. Efficient e-h separation is only possible if TiO_2 and Bi_2S_3 are connected by an epitaxial crystallographic relation. The absorbance features of Bi_2S_3 highly depend upon its dimension. Zero dimensional Bi_2S_3 nanodots are capable of only absorbing the UV light for the strong 3D quantum confinement effect. Whereas 1-D nanowire/rod and 2-D nanosheet morphology can absorb in broad spectrum area from visible (VIS) to near infrared (NIR) region [23,24]. So, for the maximisation of photocatalytic property of $\text{Bi}_2\text{S}_3/\text{TiO}_2$ NHS, exact morphology with epitaxial growth of one onto another is highly necessary. One dimensional structure can offer a direct path for the photogenerated charges, resulting in superior charge transport properties for large surface area. Previous result also suggests [25] that hierarchical morphology is facile for dye adsorption as they have high surface area.

Here we have synthesized Bi_2S_3 nanourchin by the self assembly of Bi_2S_3 nanorods. Controlled synthesis and suitable use of additives resulted in a highly monodispersed Bi_2S_3 nanourchin. $\text{Bi}_2\text{S}_3/\text{TiO}_2$ NHS has been synthesized by two step process. Hydrothermal treatment of Bi_2S_3 nanourchin with Ti-precursor resulted in $\text{Bi}_2\text{S}_3/\text{TiO}_2$ NHS, where anatase TiO_2 NCs is uniformly anchored.

From our previous research and literature survey [25–28], we have found another way to maximise the photoactivity of semiconductor is the attachment of metal nanocrystals. Metal NCs can act as an electron sink and can accept photogenerated electrons from semiconductor resulting in the increment of exciton life time. Our recent research predicts [25,26] that formation of metal-semiconductor epitaxy formation is crucial for efficient charge separation. Metal NCs can often extend the light absorption of semiconductor. Localised surface plasmon resonance (LSPR) corresponds to the collective oscillation of surface electrons with an

oscillation frequency that depends upon metal nanocrystal size, shape and degree of alloying. Metal nanocrystals can act as a nanoantenna which can enhance electric field at the surrounding (0–40 nm) medium. As the optical absorbance of semiconductor depends on intensity of the perturbation electric field, so presence of metal NC in close vicinity can enhance absorbance intensity. The enhanced energy due to plasmon in metal can be transferred directly by transfer of electrons to semiconductors ('hot' electron). Another mechanism is plasmon induced resonance energy transfer (PIRET). In PIRET, the plasmonic resonance excites electron-hole pairs in the semiconductor by coupling between the plasmonic dipole in the metal and electron-hole pair dipole of semiconductor.

Enhancement of photoactivity is already observed in ternary heterostructures composed of QDs, metal NCs and oxide semiconductor nanoparticles [29]. The plasmonic photosensitization effect in our developed $\text{Bi}_2\text{S}_3/\text{TiO}_2$ is not reported yet. We have also studied the photo conversion enhancement by altering the Au nanoparticles size/shape in these newly formed ternary structures to get beyond the best result.

2. Experimental section

2.1. Materials

Bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), sodium diethyldithiocarbamate ($\text{Na}[\text{S}_2\text{CNET}_2]$), ethanol, oleic acid (OA), chloroauric acid, tetrachloroethelene (TCE), toluene, rhodamine B (RhB) dye, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), diphenylcarbazide, citric acid, acetone all reagents were of analytical grade and purchased from MERCK. Oleylamine (OLAM), titanium butoxide, dodecanthiol, tri ethylorthosilicate (TEOS), butylamine were purchased from Sigma Aldrich. All reagents were used as purchased without further purification. DI water was used throughout all the experiments.

2.2. Preparation of bismuth diethyldithiocarbamate complex ($\text{Bi}(\text{S}_2\text{CNET}_2)_3$)

In a typical synthesis procedure 3.39 mmol of Bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was dissolved in 25 ml of ethanol to form a homogeneous solution. Then, 40 ml ethanol solution containing 10 mmol sodium diethyldithiocarbamate ($\text{NaS}_2\text{CNET}_2$) was added dropwise to the previous solution under vigorous stirring. A bright yellow colloid suspension was formed instantly. After 2 h of vigorous magnetic stirring the yellow colored precipitate was collected by centrifugation. The powder was dried for 4 h at 60°C before further use.

2.3. Preparation of bismuth sulfide (Bi_2S_3) nanorods assembly

Bismuth sulfide nanorod assembly was synthesized by decomposition of bismuth diethyldithiocarbamate complex in a mixed solvent of oleylamine (OLAM) and oleic acid (OA). In a typical synthesis procedure 0.17 mmol of bismuth diethyldithiocarbamate, 1.5 ml of OLAM, 4 ml of OA, 0.523 ml of dodecanthiol were mixed in 25 ml round bottom three neck flask fitted with a reflux condenser. The system was evacuated for 15 min at room temperature. After that the temperature was increased to 90°C slowly under constant evacuation condition. Then N_2 gas was purged into the solution and the temperature was increased to 160°C and the reaction was continued for another 15 min. The black colored solution was then cooled down to room temperature and washed with toluene and excess ethanol. The product was centrifuged at 10,000 rpm for 3 min and the centrifugation was repeated for 3–4 times to remove impurities. The product was redispersed in nonpolar solvent like TCE, toluene etc.

2.4. Preparation of $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructures

$\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructures were synthesized through a simple hydrothermal procedure. In a typical reaction, 35 mg of Bi_2S_3 was dispersed in a mixed solvent containing 3 ml of toluene, 2.6 ml of OA, 1.8 ml of OLAM, 8 ml of ethanol. Then 0.463 ml of titanium butoxide was added to the mixed solution. The mixed solution was treated by sonication for 5 min and then transferred into a Teflon-lined stainless steel autoclave, heated at 180°C for 24 h. The autoclave was air-cooled to room temperature. The obtained black powders were centrifuged and washed thoroughly with ethanol and dried at 50°C for 12 h. The composition of $\text{Bi}_2\text{S}_3/\text{TiO}_2$ was varied by changing the mole percentage ratio of Bi:Ti. Three nanoheterostructures NHS1, NHS2, NHS3 were synthesized where Bi:Ti ratio were 1:0.5, 1:1.33 and 1:4 respectively.

2.5. Preparation of $\text{Au@Bi}_2\text{S}_3/\text{TiO}_2$ heterostructure

Gold nanoparticle decorated $\text{Bi}_2\text{S}_3/\text{TiO}_2$ composite was prepared using a facial method. In this procedure 35 mg of composite was dispersed in 5 ml of toluene in a 25 ml round bottom flask with a condenser. 0.033 gm of chlorauric acid dissolved in 1 ml of toluene and 0.6 ml of OLAM was used as gold stock solution and it was added to the above mixed solution. The solution was stirred for 10 min at room temperature. Then the temperature was increased to 70°C and kept at this temperature for 15 min. The solution was then cooled to room temperature and collected by centrifugation by adding excess ethanol.

3. Characterization

The crystalline phases of the products were determined by X-ray powder diffraction (XRD) by using a Bruker AXS D8SWAX diffractometer, with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$), employing a scanning rate of 0.5° S^{-1} in the 2θ range from 20° to 60° . For XRD measurement the TCE solution of the NCs was drop cast over an amorphous silicon sample holder till a thin layer visible to the naked eye was formed. Transmission electron microscopy (TEM) images, high angle annular dark field scanning TEM (HAADF-STEM) images and energy dispersive spectra (EDS), elemental mapping were taken using an ultra-high resolution field emission gun transmission electron microscope (UHR-FEG TEM, JEM-2100F, Jeol, Japan) operating at 200 kV. For the TEM observations, the sample was dissolved in TCE and was drop cast on a carbon coated copper grid. The room temperature optical absorbance of the samples was measured by a Varian Cary 5000 UV-VIS-NIR spectrometer. Room temperature photoluminescence (PL) measurements were carried out with a fluorescence spectrometer (Hitachi, F-2500). Valence state analysis was carried out by an X-ray photoelectron spectroscopic (XPS, Omicron, model: 1712-62-11) method. XPS measurements were done using an Al-K α radiation source under 15 kV voltage and 5 mA current. For XPS measurements the hexane solution of NCs was drop cast over a Si chip ($2 \text{ mm} \times 2 \text{ mm}$) till a naked eye visible thin layer was formed.

4. Photocatalytic test

4.1. Photocatalytic degradation test of rhodamine B

For the photocatalytic degradation of RhB, 10 mg of sample was dispersed in 3 ml of toluene. In another vial 10 ml of 0.0008 mM aqueous solution of RhB was prepared. After that solution containing catalyst was poured into the aqueous solution of dye. Then the bi-phasic mixture was stirred for 5 min in dark for equilibrium mixing. Then the solution was irradiated with a light source (KRATOS,

Analytical instruments, universal arc lamp supply: 250 W, 150XE, model no. 1152). The aqueous part of the bi-phasic mixture was collected at a regular interval of time and centrifuged. The absorbance measurement of the solution was conducted using a Varian Cary 5000 UV-VIS-NIR spectrophotometer. The photocatalytic experiment of RhB was also conducted in presence of selective excitation wavelength using light emitting diode (LED) to identify contribution of individual semiconductor.

4.2. Reduction of 4-nitrophenol

For the reduction of 4-nitrophenol (4-NP), 15 ml 0.01 mM aqueous solution of 4-NP was prepared. A freshly prepared aqueous solution of NaBH_4 (0.162 gm) was added to the aqueous solution of 4-NP. After that 6 mg of catalyst was added to start reaction. The absorbance measurements were carried by the same procedure as described in case of RhB.

4.3. Detection of Cr(VI)

In a typical experiment, 5 ml of a 10 ppm solution of chromium (Cr(VI)) was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ salt in DI water. Next, 0.39 mM citric acid was added to the Cr(VI) solution, followed by maintaining a constant pH of 2 using a 1 M HCl solution. A violet color was developed in the Cr(VI) solution via the addition of a 19.77 mM diphenylcarbazide solution in acetone. After color change, 2 mg of catalyst was added to the solution, and the resulting mixture was ultrasonicated for 4 min followed by incubation in the dark for 30 min under stirring to achieve adsorption-desorption equilibrium. Then the reaction mixture was irradiated with the light source previously mentioned. The reaction mixture was discarded at various interval of time and centrifuged. The concentration of Cr(VI) was measured with a spectrophotometer at $\lambda = 540 \text{ nm}$ (Varian Cary 5000 UV-VIS-NIR spectrophotometer) using the diphenylcarbazide method.

5. Electron spin resonance (ESR) spectroscopy

The ESR measurements of spin label 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were carried out at 77 K by JEOL (JES FA200) spectrophotometer using X-band (9.8 GHz) microwave source. 500 μl of control or sample solutions in toluene were put in quartz capillary tubes which were then sealed. The capillary tubes were put into the ESR cavity, and the spectra were obtained after 10 min of irradiation.

6. Device fabrication

Thin films for photocatalytic test were prepared by a multi step process. First of all glass substrates ($1 \text{ cm} \times 1 \text{ cm}$) were cleaned by standard protocol and after that they were ultra sonicated for 15 min in a mixture of acetone and isopropyl alcohol. After that the substrates were dried in 60°C in a hot air oven.

Au nanoparticles (Au NP) and Au nanorods (Au NR) were synthesized by previously mentioned method [30,31]. Long chain of ligands of gold nanoparticles (Au NP), $\text{Bi}_2\text{S}_3/\text{TiO}_2$ composites was replaced by ligand exchange process. For this 0.5 ml of butylamine dissolved in 3 ml of acetonitrile and the 3 ml of sample solution in hexane was added to it. After that the mixture was sonicated for 5 min and centrifuged. Then they were dispersed in hexane. Long chain of cetyl trimethylammonium bromide (CTAB) capped gold nanorods (Au NRs) were removed by 20 min centrifugation and finally dispersed in hexane.

1 mg of Au NP/Au NR dispersed in hexane was spin casted onto the glass substrates to form a 2D array of gold nanoparticles. After

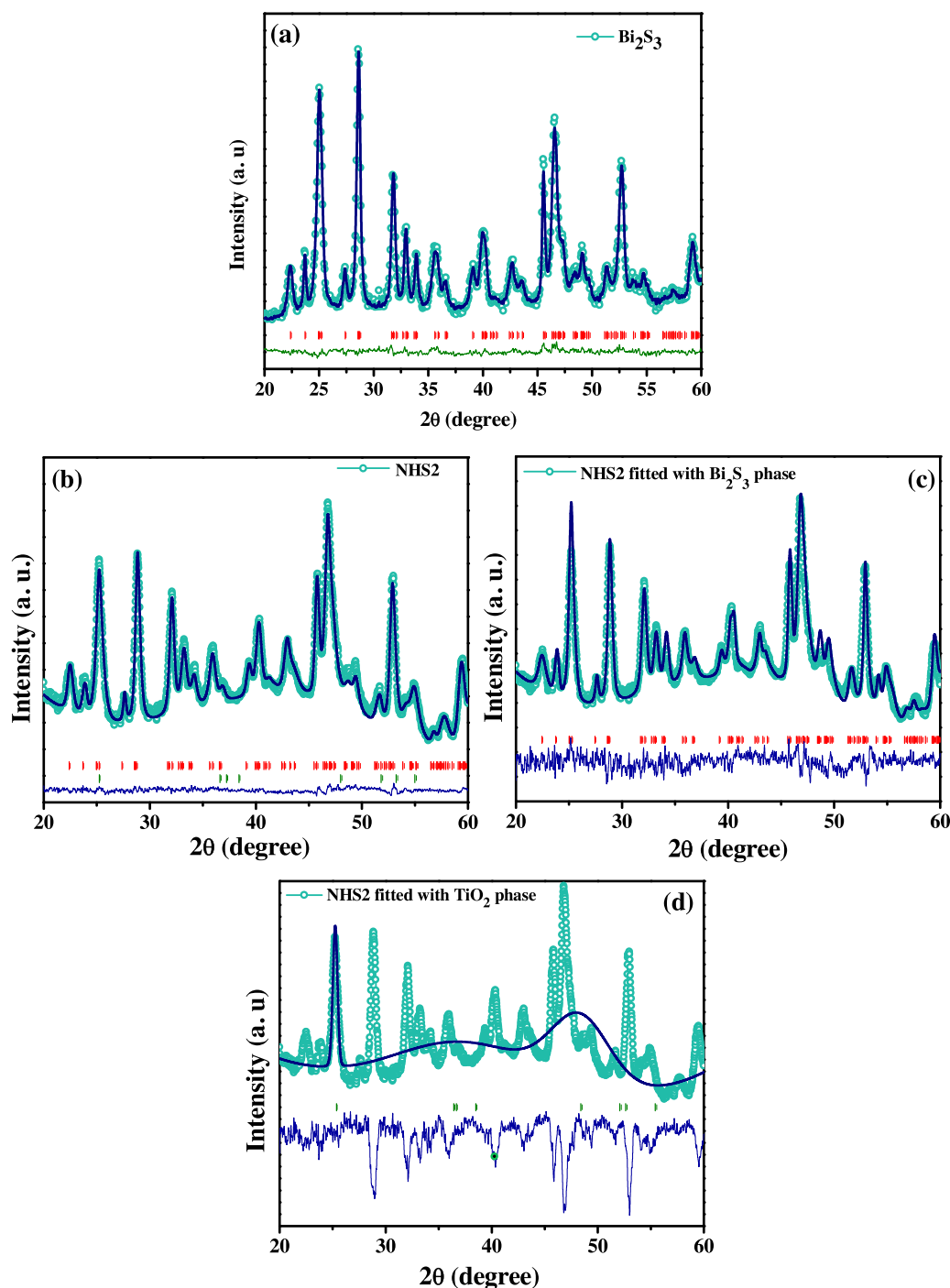


Fig 1. Typical Reitveld Refinement output pattern of $\text{Bi}_2\text{S}_3/\text{TiO}_2$ nanoheterostructures. (a) Orthorhombic pure Bi_2S_3 phase only. (b) fitted by NHS2 only. (c) XRD of NHS2 fitted with Bi_2S_3 phase only. (d) XRD of NHS2 fitted with TiO_2 only.

that the gold layer was functionalized by depositing a thin layer of tri ethylorthosilicate (TEOS). 20 μl of TEOS solution in methanol in 1% (v/v) was spin casted onto the thin layer of gold. TEOS here acted as an anchoring agent as well as a dielectric layer. After that 1 mg sample ($\text{Bi}_2\text{S}_3/\text{TiO}_2$ composites) dispersed in toluene were spin casted above each of the thin film device.

Now, in order to test photocatalytic activity of our device, it was illuminated with different light such as UV light, red LED, green LED lights. Samples for photocatalytic degradation of RhB 40 μl of methanolic solution of RhB (0.0008 mM) was drop casted upon the device and dried the device at 90°C at hot air oven. All the experiments were done in presence of air as oxygen acts as an electron

scavenger. Now to evaluate photocatalytic activity, the samples discarded for regular interval of time and their excitonic spectra were recorded by a Varian Cary 5000 UV-VIS-NIR spectrophotometer.

7. Results and discussion

7.1. XRD analysis

Phases of the as prepared Bi_2S_3 nanorod (NR) assembly, TiO_2 NPs, $\text{Bi}_2\text{S}_3/\text{TiO}_2$, $\text{Au}@ \text{Bi}_2\text{S}_3$ and $\text{Au}@ \text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructures were identified by XRD analysis. Fig. 1a shows the XRD pattern of Bi_2S_3 NR assembly, with all peaks correspond to orthorhombic

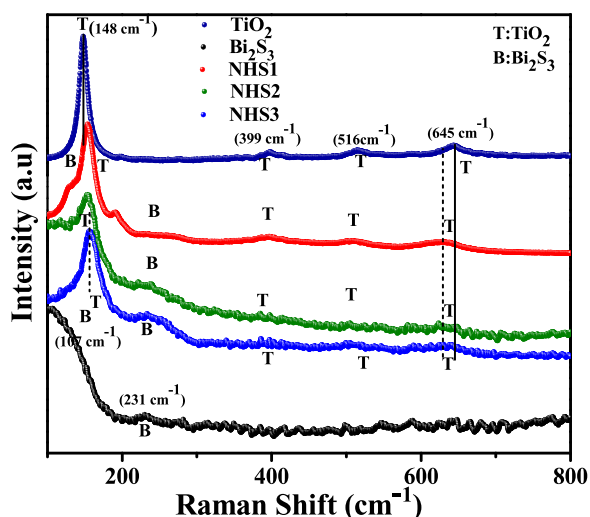


Fig. 2. Raman spectra of different nanoheterostructures.

Bi_2S_3 (JCPDS file No: 43-1471, space group $Pnma$, lattice parameters $a = 11.305 \text{ \AA}$, $b = 3.981 \text{ \AA}$, $c = 11.147 \text{ \AA}$). Rietveld refinement of XRD pattern for Bi_2S_3 NR assembly suggests that the lattice parameters, are: $a = 11.306 \text{ \AA}$, $b = 3.985 \text{ \AA}$ and $c = 11.158 \text{ \AA}$ slightly larger than the bulk value (Table S1). The unit cell volume of NRs increases from 501.67 \AA^3 to 502.71 \AA^3 as the particle size reduces to nano-size regime. The diffraction peaks of pure TiO_2 NPs shown in the supporting information (SI) Fig. S1a, identified as the tetragonal anatase TiO_2 (JCPDS file No: 84-1285, space group $I4_1/amd$, lattice parameters $a = 3.776 \text{ \AA}$, $c = 9.486 \text{ \AA}$). The XRD pattern of $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructures (SI Fig. S1b and S1c) is almost similar to that of Bi_2S_3 except the relative intensity of the peaks at $2\theta = 25.1^\circ$ (310) plane and 28.5° (121) plane of pure Bi_2S_3 . This variation in the intensity of (310) and (121) plane is due to the overlapping of (310) plane of Bi_2S_3 and (101) plane (at $2\theta = 25.3^\circ$) of TiO_2 .

The XRD pattern of $\text{Au@Bi}_2\text{S}_3$ and $\text{Au@Bi}_2\text{S}_3/\text{TiO}_2$ (SI, Fig. S1d) reveals a peak at $2\theta = 38.2^\circ$ which corresponds to (111) plane of face centered cubic (fcc) Au (JCPDS file No:01-1174). In brief,

the ternary composite material consists of fcc Au, anatase TiO_2 and orthorhombic Bi_2S_3 . Moreover XPS spectra were obtained to further investigate the presence of Au in the nanoheterostructure Au@NHS2 (NHS2 implies $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructure where $\text{Bi}:\text{Ti} = 1:1.33$). Fig. S2a in SI shows the XPS spectra of Au 4f. Two well resolved peaks at 84.0 eV and 87.7 eV are consistent with the binding energies of Au $4f_{7/2}$ and Au $4f_{5/2}$ respectively with a separation of 3.7 eV. These values confirm that gold is present in the nanoheterostructure in the metallic Au(0) state [32]. To investigate the structural overlapping of two phases in a multiphase material, Rietveld analysis is an useful method. We can see a high intensity mismatch when XRD pattern of NHS2 (Fig. 1b) was fitted with orthorhombic Bi_2S_3 and tetragonal TiO_2 separately (Fig. 1c and d). But the poor Rietveld refinement data significantly improves when we consider 80 vol% of Bi_2S_3 and 20 vol% of TiO_2 . This good fitted data suggest that there must be an overlapping of (310) plane of Bi_2S_3 and (101) plane of TiO_2 .

8. Raman spectroscopy

To further identify the individual phases and crystallinity of the as prepared samples Raman Spectra were collected in the wavenumber range $100\text{--}800 \text{ cm}^{-1}$ as shown in Fig. 2. The Raman peaks are indicated by letter 'T' for TiO_2 and letter 'B' for Bi_2S_3 . There are four Raman active modes of orthorhombic Bi_2S_3 : A_g , B_{1g} , B_{2g} and B_{3g} and one IR active mode B_{3u} which have been theoretically calculated by Tanner et al. [33]. The Raman spectrum of pure Bi_2S_3 reveals a broad hump in between 100 and 200 cm^{-1} and a short hump at 231 cm^{-1} which corresponds to theoretically predicted A_g optical phonon mode of Bi_2S_3 , associated with the transverse phonon modes. Bi_2S_3 is well known for its low thermal conductivity [34] and therefore we obtained the Raman spectra at lower laser power. Raman features of Bi_2S_3 are very sensitive to thermal power and at low excitation power these modes are indistinguishable or appeared as broad hump [33]. We noticed that in case of pure TiO_2 , there are four characteristic Raman peaks appeared at 148 cm^{-1} , 399 cm^{-1} , 516 cm^{-1} and 645 cm^{-1} . It confirms that typical anatase TiO_2 phase has been formed. The peaks at 148 cm^{-1} and 645 cm^{-1} are the characteristic E_g peaks which arise due to the symmetric stretching vibration of O-Ti-O in TiO_2 . The peak

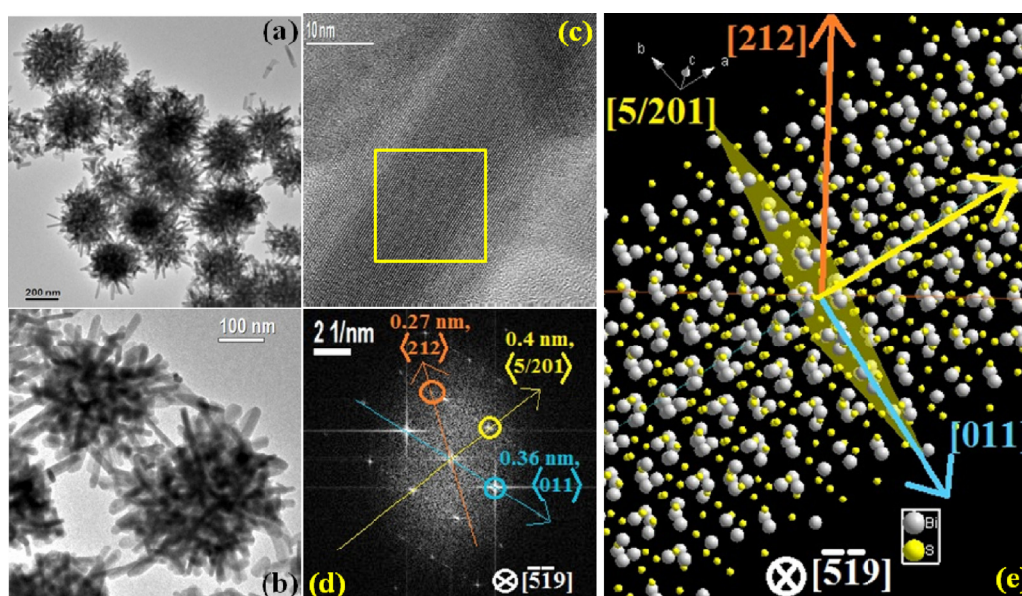


Fig. 3. (a) Large area TEM image of pure Bi_2S_3 nanorod assembly. (b) A closer view of two nanorods assembly. (c) HRTEM image of one nanorod. (d) FFT pattern of yellow square area in (c). (e) Atomic arrangement of the nanorods. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

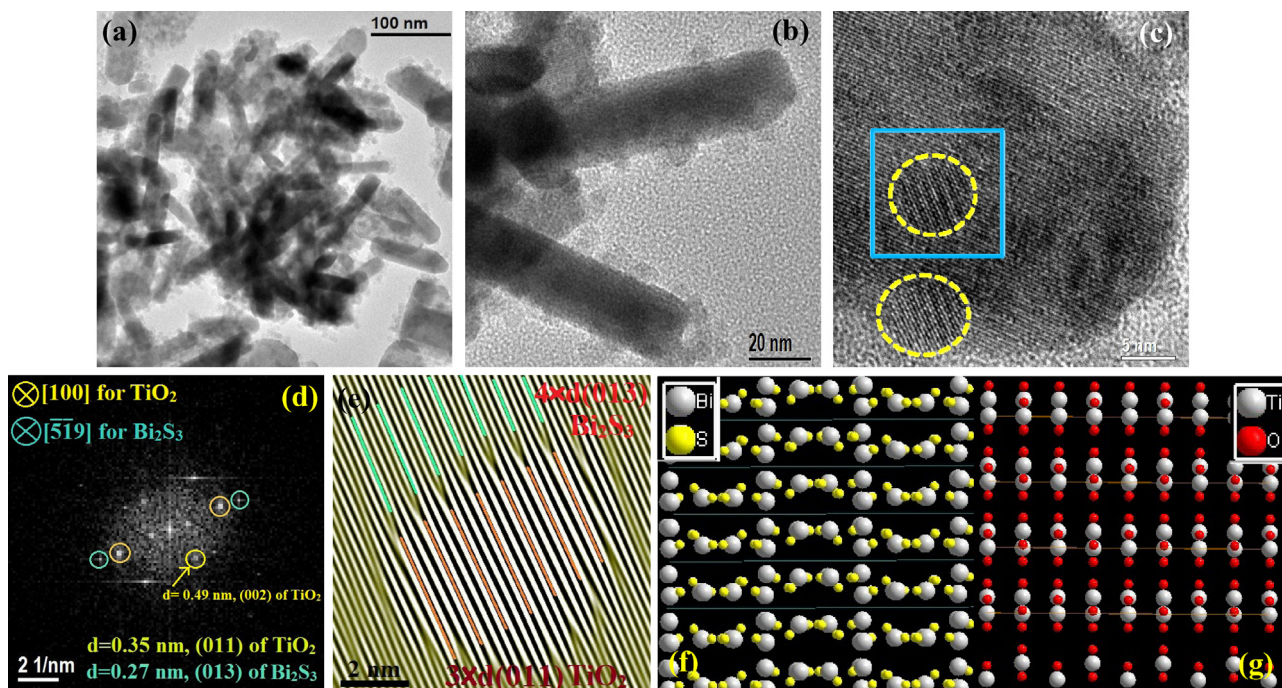


Fig. 4. (a) TEM image of NHS2. (b) A closer view of a nanorods decorated with a number TiO₂ nanoparticles. (c) HRTEM image of the nanorods with two TiO₂ nanoparticles showing by yellow circles. (d) FFT pattern of the blue square region. (e) Reconstructed HRTEM image shows that Bi₂S₃ (013) plane and TiO₂ (011) plane along the same direction. (f)–(g) Atomic model of Bi₂S₃ and TiO₂ showing same direction of growth. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

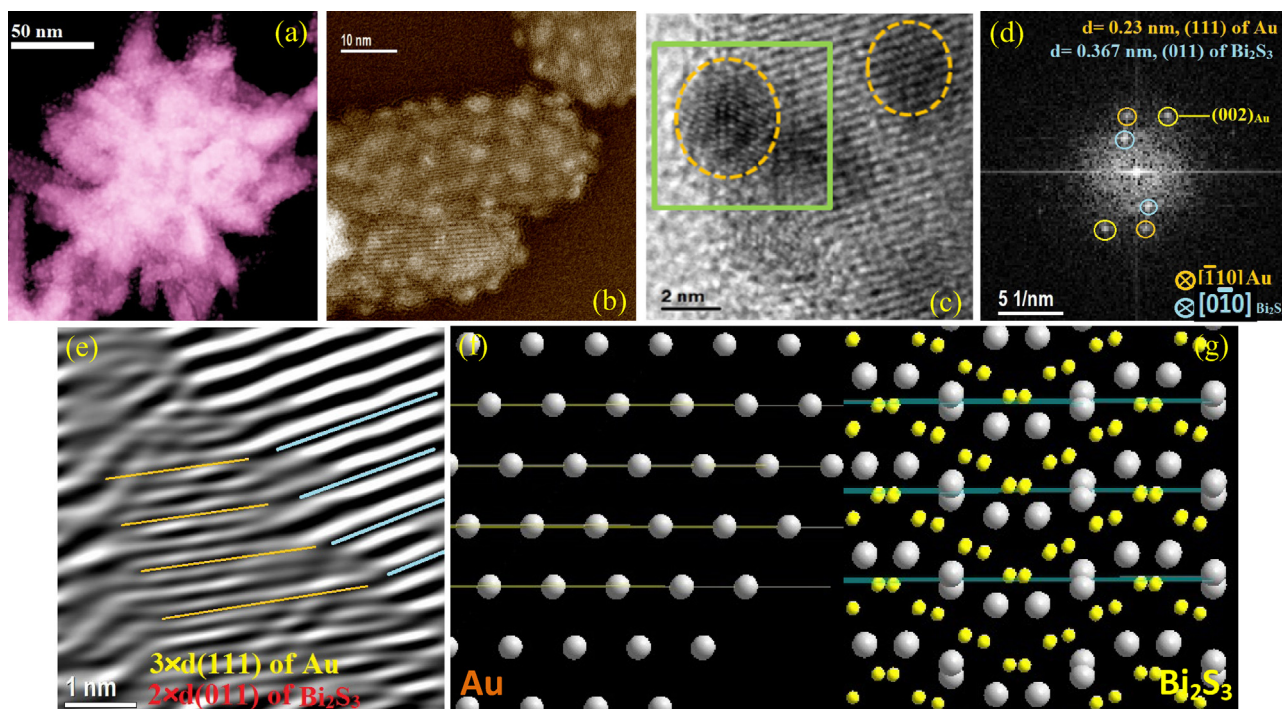


Fig. 5. (a) Dark field TEM image of Au decorated Bi₂S₃ nanorod assembly. (b) Closer view of nanorods assembly which shows two nanorods with uniform Au decoration. (c) TEM image of a nanorod with 3–4 Au particle decoration. (d) FFT pattern of green squared area in (c). (e) Reconstructed HRTEM image showing same direction of growth of (111) plane of Au and (011) plane of Bi₂S₃. (f)–(g) Atomic model showing the matching of $3 \times d(111)$ of Au and $2 \times d(011)$ of Bi₂S₃. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

at 399 cm^{-1} corresponds to B_{1g} vibrational mode caused by symmetric bending vibration of O–Ti–O and 516 cm^{-1} corresponds to A_{1g} vibrational mode arising due to antisymmetric bending vibration. The Raman spectra of Bi₂S₃/TiO₂ composites consist of both Raman peaks of Bi₂S₃ and TiO₂ phases. It is very interesting that

the Raman spectra of Bi₂S₃/TiO₂ heterostructures contain a small peak around 123 cm^{-1} and the peak at 237 cm^{-1} becomes more prominent. The peak at 123 cm^{-1} is not a Raman active mode but an IR active phonon mode (B_{3u}). In general IR active mode does not appear in Raman spectrum but this IR-active to Raman-active

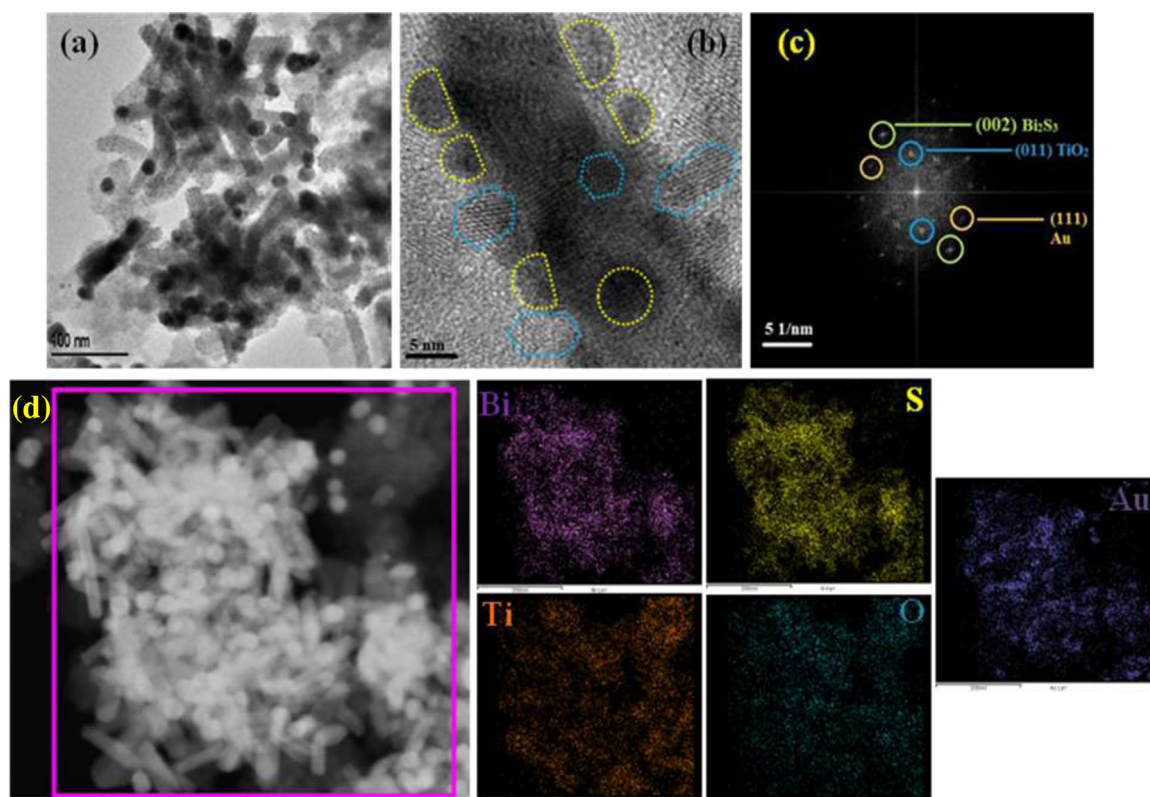


Fig. 6. TEM image of two nanorods assembly decorated with both TiO_2 and Au nanoparticles. (b) HRTEM image showing a Bi_2S_3 nanorod with a number of Au (yellow color) and TiO_2 (blue color) particle decoration. (c) FFT pattern shows the presence of three phases Bi_2S_3 , TiO_2 and Au. (d) EDS elemental mapping over two assemblies. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

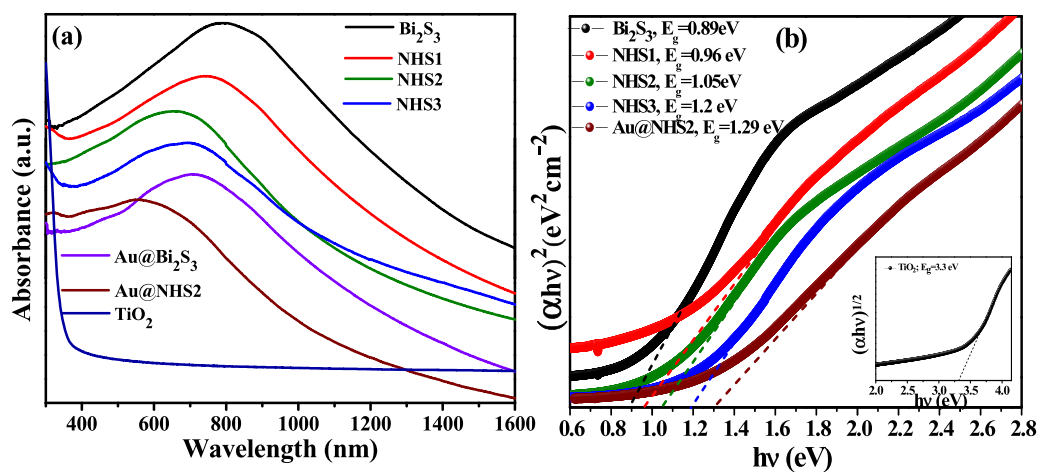


Fig. 7. (a) Absorbance spectra of pure Bi_2S_3 , pure TiO_2 and their nanoheterostructures. Absorbance edge of Bi_2S_3 shifts towards lower wavelength on heterostructure formation. (b) Tauc plot of different samples showing change of band gap. Inset shows indirect band gap of anatase TiO_2 .

transition occurs generally due to breaking of symmetry in the nanostructure material due to random displacement of defects in the lattice [35]. An interesting observation we get from the Raman spectrum is that E_g peak of TiO_2 at 148 cm^{-1} gradually shifts to higher wavenumber. However, E_g peak at 645 cm^{-1} shifts towards lower wavenumber. It indicates that there must be an interaction between Bi_2S_3 and TiO_2 and the crystalline defect states of TiO_2 are modified due to composite formation (as TiO_2 is epitaxially connected to the Bi_2S_3 which will be discussed in the TEM analysis section). The crystalline defects can change the vibrational mode of TiO_2 , it can act as a trap to capture photo generated electron resulting in an electron–hole separation which is beneficial for pho-

tocatalytic activity. We also notice that the intensity of both TiO_2 and Bi_2S_3 drastically decreases and broadens for the composites. This can be a result of scattering loss due to defects formation at the interface between Bi_2S_3 and TiO_2 , especially the E_g peak of TiO_2 at 148 cm^{-1} is present in all the composites but it is broadened and blue shifted. The E_g mode of TiO_2 associated with O–O interactions which makes it more sensitive to make oxygen vacancy [36]. Lattice defect such as the removal of an oxygen atom from its lattice position makes the bond weak and shifts the neighboring titanium atom to their mean position and as a result of it the band is blue shifted [37]. Specifically, the band broadening and shifting to higher wavenumber is associated with lattice contraction which is a result

of oxygen vacancy formation [38]. The oxygen vacancy formation of the $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructure was confirmed from XPS analysis. An XPS spectrum of O 1s (SI, Fig. S2b) was resolved into three peaks at 530.5 eV, 532.9 eV and 533.8 eV respectively. The peak at 530.5 eV arises due to Ti–O bond formation and on the other hand the other two peaks correspond to oxygen vacancy or defects and chemically adsorbed species such as H_2O [39]. The relative intensity of the peak at 533.8 eV related to chemically adsorbed H_2O is too low compared to the other peaks. Hence the contribution of H_2O molecules is negligible. The peaks at 459.2 eV and 465 eV correspond to the XPS peaks of Ti $2p_{3/2}$ and Ti $2p_{5/2}$ respectively for anatase TiO_2 (SI, Fig. S2c). Each peak can be resolved into two peaks which suggest the presence of both Ti^{4+} and as well as Ti^{3+} state. Thus we can conclude that direct contact between TiO_2 and Bi_2S_3 modifies the surface states of both Bi_2S_3 and TiO_2 .

8.1. TEM analysis

Fig. 3a shows the large area TEM image of as-synthesized nanourchin of pure Bi_2S_3 by colloidal process. The nanourchins are $\sim 200 \pm 20$ nm in size with monodisperse in nature and good colloidal stability in organic solvent. Closer view of two nanourchins in Fig. 3b demonstrates self assembly of nanorods. Fig. 3c and Fig. 3d shows the HRTEM and FFT pattern of a typical type nanorod. From the FFT pattern, we have assigned the plane as (5/201) with d-spacing 0.4 nm, (212) with d-spacing 0.27 nm and (011) with d-spacing 0.36 nm when viewed along $\sim [\bar{5}\bar{1}9]$ zone axis. The main reason for growth along [5/201] direction is again presence of a permanent dipole along this direction for alternative array of 2- S rich layer and 1- Bi rich layer. For this case, after the nucleation Bi_2S_3 nuclei might grow along polar direction [011] and [5/201]. The (5/201) plane is S-rich and undergoes stabilisation by NH_2 -group of OLAM by electron donation of amine to sulphur empty shell. Atomic arrangement of Bi and S under $[\bar{5}\bar{1}9]$ zone axis is shown in Fig. 3e. We have identified that some of the Bi_2S_3 nanorods were grown along another zone axis [0 $\bar{1}$ 0]. Fig. S3a and Fig. S3b shows the HRTEM image and the corresponding FFT pattern of a single nanorod respectively. Two perpendicular planes with d-spacing value 0.52 nm and 0.37 nm were identified as (200) and (011) planes.

To get more inside for formation mechanism we have varied the reaction condition especially the ratio of two capping agents. The decomposition of $\text{Bi}(\text{S}_2\text{CNET}_2)_3$ in pure OLAM in presence of 1-dodecanthiol (1-DDT) (no oleic acid) results in the formation of only Bi_2S_3 nanorods (SI, Fig. S4a) with poor size distribution and variable aspect ratio. Use of 0.5 ml oleic acid (OA) with fixed amount of OLAM and 1-DDT favors the formation of some Bi_2S_3 nanorod assembly but complete 3D nature is not there (SI, Fig. S4b). We have found that with increase of OA concentration, the assembly size gradually increases and a complete 3D urchin like morphology can be achieved (SI, Fig. 4f). With controlling the amount of OA we can control nanourchin size from 150 nm to 500 nm. Increase of OLAM concentration (in absence of OA) decreases the nanorod size. So OLAM here acts as nucleating agent to initiate the decomposition of $\text{Bi}(\text{S}_2\text{CNET}_2)_3$ complex and capping agent for specific Bi and S rich polar facets but do not play a crucial role in assembly formation. Use of OA results in a limited ligand protection on the surface of nanorods. The formation of amide bond by reaction between amine group of OLAM and acid group of OA at reaction temperature might decrease the capping efficiency of OLAM which accelerates the hierarchical shape formation [40–42].

Fig. 4a depicts the TEM images of $\text{Bi}_2\text{S}_3/\text{TiO}_2$ NHS2 (at Bi: Ti = 1: 1.33) where nanourchin is found to be decorated with TiO_2 nanocrystals. Large area TEM image [in SI, Fig. S5] shows that each of nanourchins is well decorated with TiO_2 NCs. Closer view in Fig. 4b over 2–3 nanorods demonstrate that each nanorod is decorated

with multiple number of TiO_2 nanocrystals. The low contrast of TiO_2 NCs might be for low thickness of NC and lower Z value than that of Bi_2S_3 . Fig. 4c shows the HRTEM image of the tip area of nanorod where two TiO_2 NCs are situated. Fig. 4d shows the FFT pattern obtained from the blue colored square area of Fig. 4c. The spots appearing in FFT originate from the planes of both Bi_2S_3 and TiO_2 phases. The d-values obtained from two yellow circled spots are 0.49 nm and 0.35 nm which are assigned as (002) and (011) plane of TiO_2 respectively. The calculated zone axis for viewing TiO_2 NCs is [100]. The zone axis for Bi_2S_3 is $[\bar{5}\bar{1}9]$ which was also assigned same as for pure Bi_2S_3 nanorods. The d-value obtained from cyan color spot which is also along the same direction of (011) plane of TiO_2 is found to 0.27 nm, which is the reflection of (013) plane of Bi_2S_3 . The growth of (011) plane of TiO_2 along the same direction of (013) of Bi_2S_3 is an indication of epitaxy between these two planes. Fig. 4e shows the reconstructed HRTEM image by masking the two highlighted spots in Fig. 4d which also clearly shows the epitaxy along the [013] direction of Bi_2S_3 NRs. The cyan and red colored lines are indicated for the Bi_2S_3 and TiO_2 parts respectively for better visibility of coincidence of planes. Although the large d-value difference in between (011) TiO_2 and (013) Bi_2S_3 is there. So, large lattice mismatch is present if one compare the matching of one (011) plane with (013) plane. But the reconstructed HRTEM revealed that periodic arrangement of $4 \times d(013)$ ($= 1.08$ nm) of Bi_2S_3 matches exactly with $3 \times d(011)$ ($= 1.05$ nm) of TiO_2 which results in minimum lattice mismatch between Bi_2S_3 and TiO_2 . Fig. 4f and g shows an atomic arrangement of (011) plane of TiO_2 and (013) planes of Bi_2S_3 and the match between $3d(011)$ and $4d(013)$ planes (Fig. 4e). The TiO_2 NCs which are situated at the side surface can also be related by above established epitaxial relationship (SI, Fig. S6a and b). The perpendicular facet of {013} of Bi_2S_3 is S-rich. So deposition of Ti^{4+} along with this facet is highly feasible for formation of strong covalent Ti–S bond. Atomic arrangement in Fig. 4f and g shows the position of different atoms at heterojunction.

The Bi:Ti ratio was varied to get different type of heterostructure to maximise the photocatalytic activity of heterostructure. Each nanorod is decorated with 2–3 TiO_2 NCs for Bi:Ti = 1:0.5. Excellent epitaxy has been confirmed from HRTEM (SI, Fig. S7b). Free TiO_2 NCs are formed for higher molar ratio, Bi: Ti = 1:4 instead of epitaxial growth on Bi_2S_3 . Inverted HRTEM image clearly shows the presence of both epitaxially connected and free standing TiO_2 onto Bi_2S_3 nanorod (SI, Fig. S7d).

Fig. 5a shows the STEM-DF image of Au NC homogeneously decorated on Bi_2S_3 nanourchin. Fig. 5b shows the closer view of 2–3 nanorods where multiple number of Au NCs with size $\sim 3 - 5$ nm are situated on the surface. No free standing Au NCs were found due to the Au–S eternal affinity. HRTEM image in Fig. 5c shows the co-existence of lattice fringes both from Au and Bi_2S_3 . Fig. 5d shows the FFT pattern from the green square area of Fig. 5c. We assigned the zone axis for Bi_2S_3 as [0 $\bar{1}$ 0] and for Au as [110]. We identified the (002) and (111) planes from orange and yellow circled spots. Epitaxial growth of (111) plane of Au over (011) plane of Bi_2S_3 nanorods is established from FFT analysis. Reconstructed TEM image (using Gatan Software) by masking the circular spots in FFT shows the epitaxial relationship between Au and Bi_2S_3 in Fig. 5e. Periodic arrangement of $3 \times d(111)$ ($= 0.69$ nm) of Au matches closely with $2 \times d(011)$ ($= 0.72$ nm) of Bi_2S_3 . Fig. 5f and g show the atomic arrangement of (111) plane of Au and (011) plane of Bi_2S_3 and the matching between $3d(111)\text{Au}$ and $2d(011)\text{Bi}_2\text{S}_3$ planes.

Fig. 6a illustrates the TEM image of $\text{Bi}_2\text{S}_3/\text{TiO}_2/\text{Au}$ NHSS. Each of Bi_2S_3 nanorods are found to be decorated with both TiO_2 and Au nanocrystals. Fig. 6b depicts the HRTEM image of single nanorod decorated with multiple TiO_2 and Au NCs. The highest contrast NCs are Au NCs (high Z value, marked with yellow circles) and lighter contrast NCs are TiO_2 (cyan circled). Au NCs are found to be

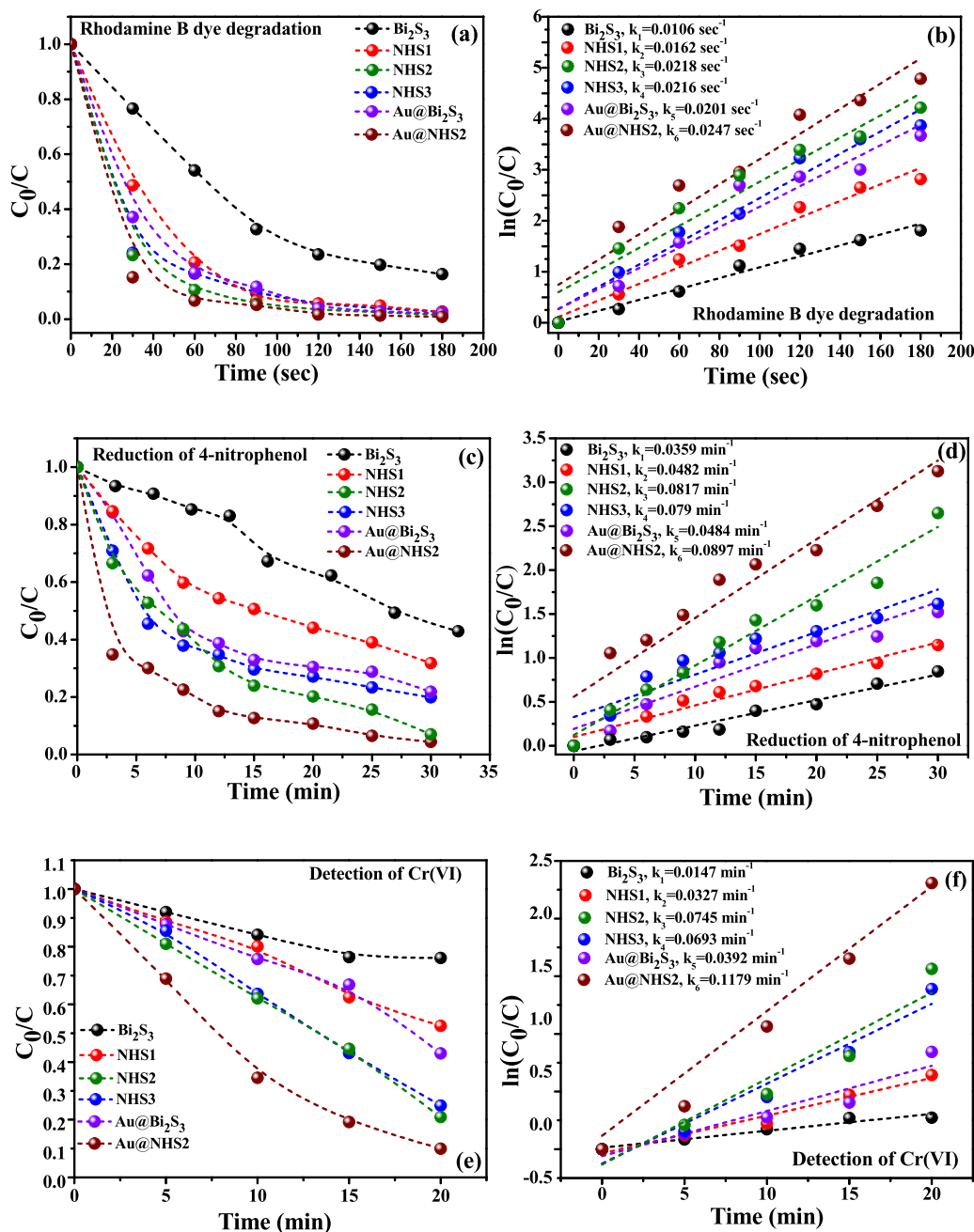


Fig. 8. Solar light driven (a)–(b) photo degradation of RhB dye. (c)–(d) photoreduction of 4-paranitrophenol. (e)–(f) detection of Cr(VI).

solely grown onto Bi_2S_3 facets without any direct contact with TiO_2 NCs. The characteristic planes of Au (111) and TiO_2 (011) obtained from FFT pattern in Fig. 6c confirm the formation of Au and TiO_2 NCs on Bi_2S_3 nanorods. Fig. 6d shows the EDS element mapping over two Au and TiO_2 decorated Bi_2S_3 nanorod heterostructures which proves homogenous distribution of respective elements on the nanorods.

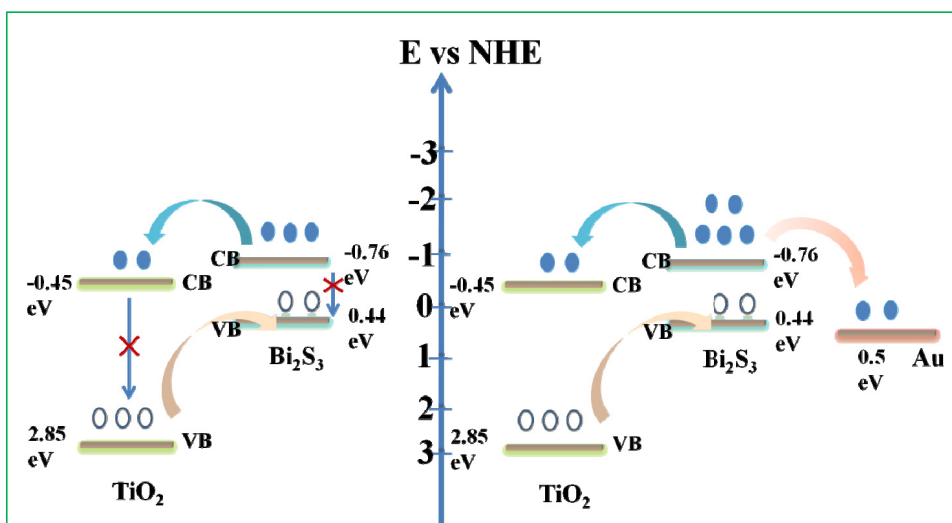
8.2. Optical properties

Room temperature UV–vis absorption spectra of Bi_2S_3 nanorod assembly, pure TiO_2 nanoparticles and $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructures in the absence and presence of Au nanoparticles are shown in Fig. 7a. A strong absorption peak centered around 800 nm is observed for pure Bi_2S_3 nanorod assembly. The absorbance feature covers the visible region and extended up to NIR region (~1600 nm)

of solar spectrum. The UV–vis absorption spectra of as synthesized TiO_2 exhibited an absorption peak at 370 nm which is the characteristic band edge absorption of anatase TiO_2 phase. The band edge absorption of Bi_2S_3 is blue shifted from 800 nm to 564 nm on heterostructure formation. The band gaps of the as synthesized samples were calculated using the equation

$$(\alpha h\nu)^n = C (h\nu - E_g) \quad (1)$$

Where α , h , ν and E_g are the optical absorption coefficient, Planck constant, photon frequency and band gap of semiconductor, respectively and C , n are constants. The value of 'n' depends upon whether the semiconductor is direct ($n=2$) or indirect ($n=1/2$) semiconductor. The indirect band gap of TiO_2 was calculated to be 3.3 eV (Fig. 7b inset). Sensitization of Bi_2S_3 nanorod assembly with TiO_2 nanoparticles extended the absorption spectra from UV to visible range up to 1500 nm. From the Tauc plot shown in Fig. 7b, the band



Scheme 1. Relative band alignment of $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructure and Au decorated $\text{Bi}_2\text{S}_3/\text{TiO}_2$ nanoheterostructure.

gap of NHS increases from 0.89 eV to 1.2 eV with increasing of TiO_2 content. $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructure is a type II heterostructure. The electron is delocalized through the entire system as its low effective mass and the small conduction band offset of 0.31 eV [43,21]. Moreover TiO_2 has a higher electron affinity of 5.1 eV than that of Bi_2S_3 (electron affinity 4.58 eV) [44,19]. Therefore the electrons are delocalized towards TiO_2 in the heterostructure. In contrast hole is more confined to Bi_2S_3 as the higher effective mass and higher valence band offset of 2.06 eV [43,21]. Due to type II heterostructure formation and lower effective hole mass of TiO_2 , holes are transferred to the Bi_2S_3 nanorods [45]. In our asymmetric heterostructure, the electrons and holes have a different level of confinement. Here electrons gain a 0-D characteristic as the electrons are transferred to spherical TiO_2 nanoparticle and the hole maintains a 1-D characteristic due to confined into the Bi_2S_3 nanorods assembly. Thus the heterostructure formation offers a different dimensionality of electrons and holes [46]. Thus the band gap absorption of Bi_2S_3 is blue shifted due to different level of confinement of electrons and holes in the heterostructure [47].

$\text{Au@Bi}_2\text{S}_3$ has an absorption band around 695 nm with a shoulder around 500 nm which arises due to Au nanoparticle (~5 nm) decorated on the nanorods assembly. The LSPR peak of Au nanoparticles is very sensitive to size, shape and the surrounding environment. Here the absorption peak due to LSPR of Au nanoparticles is not as prominent as the sizes of the Au nanoparticles are small to exhibit a proper LSPR absorbance. Epitaxially grown metal-semiconductor heterostructure gives rise to lower potential barrier and large overlap of electronic wave functions between Bi_2S_3 and Au. As a result of these, photoexcited electrons in Bi_2S_3 are transferred into interfacial states and reduce the absorbance of Bi_2S_3 consistent with earlier reported results [48].

8.3. Photocatalytic activity

In order to evaluate the photocatalytic activity of all the synthesized, RhB was used as a model dye under artificial solar light irradiation (Fig. S8a). The photocatalysis of RhB is negligible in absence of any sample. Although the degradation of RhB is fast in presence of pure Bi_2S_3 nanourchin (under solar light irradiation) but degradation in presence of pure TiO_2 NCs (4–5 nm) is very slow. TiO_2 took more than 2 h to complete degrade RhB. Nearly 75–80% RhB was found to be degraded in presence of Bi_2S_3 nanourchin just in 3 min. The rate is found to be higher than the previous reported Au- Bi_2S_3 metal semiconductor heterostructure.[28]

The enhanced reaction rate observed for pure nanourchin may be due to the increased surface area of hierarchical structures. The other nanourchins having size higher than 200 nm shows little slower photocatalytic activity probably for increase in mass of each assembly results faster sedimentation from solution before complete dye degradation. Fig. 8a shows the change of relative dye concentration in presence of different photo catalyst under white light irradiation. As the degradation was very fast, we took the aliquot in 30 s interval from the time light exposing. Initial reaction steps of all systems showed pseudo first order rate kinetics with time (t), so degradation rate constant (k) can be obtained from the linear fit of: $\ln(C/C_0) = -kt$, where C_0 and C are initial and equilibrium dye concentration at time t respectively. Fig. 8b shows the all the experiments have been done under same power density of light (0.65 mW/cm^2). So simply comparing the k values we can compare the photocatalytic activity of different samples. Nanoheterostructures which are the composites of TiO_2 and Bi_2S_3 shows higher photocatalytic activity than pure Bi_2S_3 nanourchin. Nearly 95–98% RhB is found to be degraded in presence of NHS1, NHS2 and NHS3 ($\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructures with a Bi:Ti ratio 1:0.5, 1:1.33, 1:4 respectively). Maximum rate constant is found for NHS2 ($k_3 = 0.0218 \text{ s}^{-1}$; Bi:Ti = 1:1.33). The rate constant value is more than double of pure Bi_2S_3 nanourchin. Increase of TiO_2 concentration improves the value of rate constant. But for NHS3, a little decrease of k value is obtained. Small Au NCs decorated Bi_2S_3 nanourchins also shows an enhancement of photocatalytic activity than pure Bi_2S_3 . The obtained k value for $\text{Au@Bi}_2\text{S}_3$ NHS is just twice that of pure Bi_2S_3 sample. The increase of photocatalytic activity in case of NHS might be attributed to unique nanorod/nanocrystal epitaxial heterostructure and the improved charge separation process. In order to understand the mechanism we studied the relative band alignment of Bi_2S_3 , TiO_2 and Au. The band alignment of heterostructure is shown in Scheme 1. According to previous report, the conduction band position of TiO_2 is lower than that of Bi_2S_3 . Whereas the valence band of Bi_2S_3 position is much higher than that of TiO_2 which results in a type-II band alignment. The effective charge carrier separation inside the heterostructure depends upon the relative migration rates of electrons and holes in each semiconductor. We calculated the diffusion time of photo generated charge carriers inside both the semiconductors using the following equation for charge carrier diffusivity (D):

$$D = \frac{\mu k_B T}{q_e} \quad (2)$$

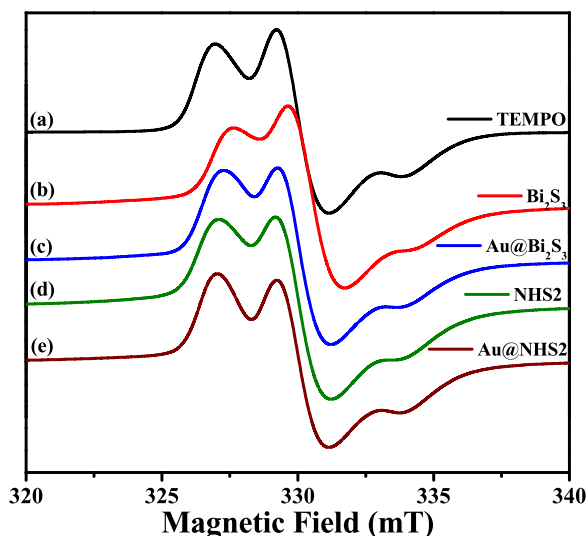


Fig. 9. The ESR signal of (a) 0.02 mM TEMPO in toluene and (b)–(e) in presence of 0.1 mg/mL of Bi_2S_3 , $\text{Au@Bi}_2\text{S}_3$, NHS2 and Au@NHS2 respectively after 10 min of irradiation.

where μ is the mobility of charge carriers, k_B is Boltzmann coefficient, T is the absolute temperature, and q_e is the charge of the electron. The diffusivities of photogenerated electrons and holes inside TiO_2 crystal are calculated to be $1 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and $4 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ respectively taking the mobility value of electrons and holes as $4 \times 10^{-5} \text{ m}^2/\text{Vs}$ and $1.6 \times 10^{-3} \text{ m}^2/\text{Vs}$ respectively at 300 K [45]. The time required for the migration of charge carriers from the centre of TiO_2 NCs to the interface region between TiO_2 and Bi_2S_3 can be determined by the formulae:

$$\tau = \frac{r_0^2}{\pi^2 D} \quad (3)$$

where r_0 is the migration length, which is taken as 2.5 nm (TiO_2 NCs size $\sim 5\text{--}6$ nm). So the calculated migration time of electron and hole are 0.6 picosec and 0.02 picosec respectively. So faster migration of hole compare to electron (nearly 30 times faster) is expected from the inside of TiO_2 NCs which results in relatively high electron density inside the TiO_2 NCs and large hole concentration at NC surface or at the interface. So hole migration is expected from TiO_2 to Bi_2S_3 nanorods.

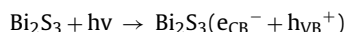
In similar process we have calculated the migration time for photogenerated carriers of Bi_2S_3 nanorods. Mobility values of electrons and holes of Bi_2S_3 were taken as $0.35 \text{ m}^2/\text{Vs}$ and $0.08 \text{ m}^2/\text{Vs}$ respectively. [49] For an 1-D nanostructure, carriers from the centre of nanorod can migrate in two perpendicular direction: migration along the width and length. As most of the TiO_2 NCs are situated onto side surfaces of Bi_2S_3 nanorods, we calculated the migration time along the width only. The migration time for electron and hole from centre of nanorods is found to be 0.07 fsec and 2.4 fsec respectively. So photoexcited electrons in Bi_2S_3 nanorods migrate much faster (~ 35 times) to the surface compare to hole in Bi_2S_3 . So transfer of photoexcited electrons from Bi_2S_3 to TiO_2 is much more facile compare to hole transfer process. So, after the photoexcitation of NHS, complete charge separation is possible which leads to high concentration of hole in Bi_2S_3 nanorods and electron rich TiO_2 .

The above explanation was further verified experimentally by taking the room temperature PL spectra of pure and NHS samples. PL spectra can be utilized to investigate the recombination rate of the photogenerated electron–hole pairs. The decrease in the recombination rate gives rise to a low PL intensity [50–52]. Fig. S9 in SI shows the PL spectra. The intensities of characteristic emission peaks of TiO_2 at 410 nm, 430 nm and 460 nm ascribed to mainly Ti^{3+}

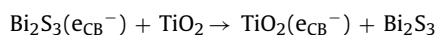
and oxygen vacancy defect states are found to be decreased with heterostructure formation which suggests improvement of charge separation.

The interface between Bi_2S_3 and Au nanoparticles makes Schottky junction due to higher electron affinity (work function) of Au. The electric field across Schottky junction enhances e–h separation. [25,26] Photoexcited electrons in Bi_2S_3 which transferred to the surface very fast, can move both to the epitaxially connected TiO_2 NCs and Au NCs as demonstrated in Scheme-I. The photogenerated electrons on the surfaces of TiO_2 and Au can react with surface absorbed oxygen molecules to produce superoxide radical anions ($\text{O}_2^{\bullet -}$). The holes on the surface of Bi_2S_3 can be transferred to the absorbed H_2O molecules to generate highly oxidising OH^{\bullet} radical according to the following redox steps:

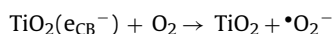
Charge separation



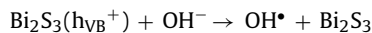
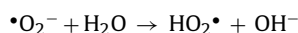
Charge transfer



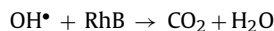
Superoxide radical ($\text{O}_2^{\bullet -}$) formation



OH^{\bullet} radical formation



Dye degradation



The formation of OH^{\bullet} radical as an active photocatalytic species during photocatalysis can be probed using terephthalic acid (TA). Reaction of TA with OH^{\bullet} radicals can generate fluorescent 2-hydroxyterephthalic acid (TAOH) which shows emission peak at 425 nm with excitation at 315 nm [50]. The fluorescence intensity of TAOH is proportional to the amount of OH^{\bullet} produced on the surface of photocatalysts. Fig. S10 in SI shows the emission of in-situ formed TAOH in water in presence of different photocatalyst when irradiated for 20 mins. Maximum fluorescence intensity of TAOH has been found for Au@NHS2 which reveals that maximum OH^{\bullet} radical formation by Au@NHS2 heterostructure at a fixed time of solar light irradiation.

We have also studied the photocatalytic reduction of 4-NP in presence of NaBH_4 . The 4-NP shows absorbance peak at about 317 nm and it has been red shifted to 405 nm in presence of NaBH_4 for formation of 4-nitrophenolate ion. Although NaBH_4 is a strong reducing agent it cannot be capable of reducing 4-nitrophenolate in presence of solar light. Presence of catalyst (nanourchin or NHSs) triggers the conversion of 4-nitrophenolate to 4-aminophenolate in presence of light irradiance. The depletion of the 4-nitrophenol peak at 400 nm and the concomitant increase of a peak at 297 nm has been monitored over time (SI, Fig. S8b). Fig. 8c shows different reduction concentration of 4-NP in presence of different photocatalyst under solar light irradiation. Fig. 8d shows catalytic rate constants obtained for different photocatalyst. The rate in presence of pure Bi_2S_3 nanourchin is $3.6 \times 10^{-2} \text{ min}^{-1}$ whereas that of the Au@NHS2 i.e. $\text{Bi}_2\text{S}_3/\text{TiO}_2/\text{Au}$ is $9.0 \times 10^{-2} \text{ min}^{-1}$. The photoexcited electrons in the semiconductors are responsible for the functional group transformation. After the photoexcitation as-generated holes undergoes neutralised by the hydrides (H^-)/electrons from BH_4^- and the electrons in CB can directly transfer to surface absorbed 4-nitrophenolate ion. Greater extent of formation of photoexcited charge carriers in Au@NHS2 results in the highest photocatalytic reduction property.

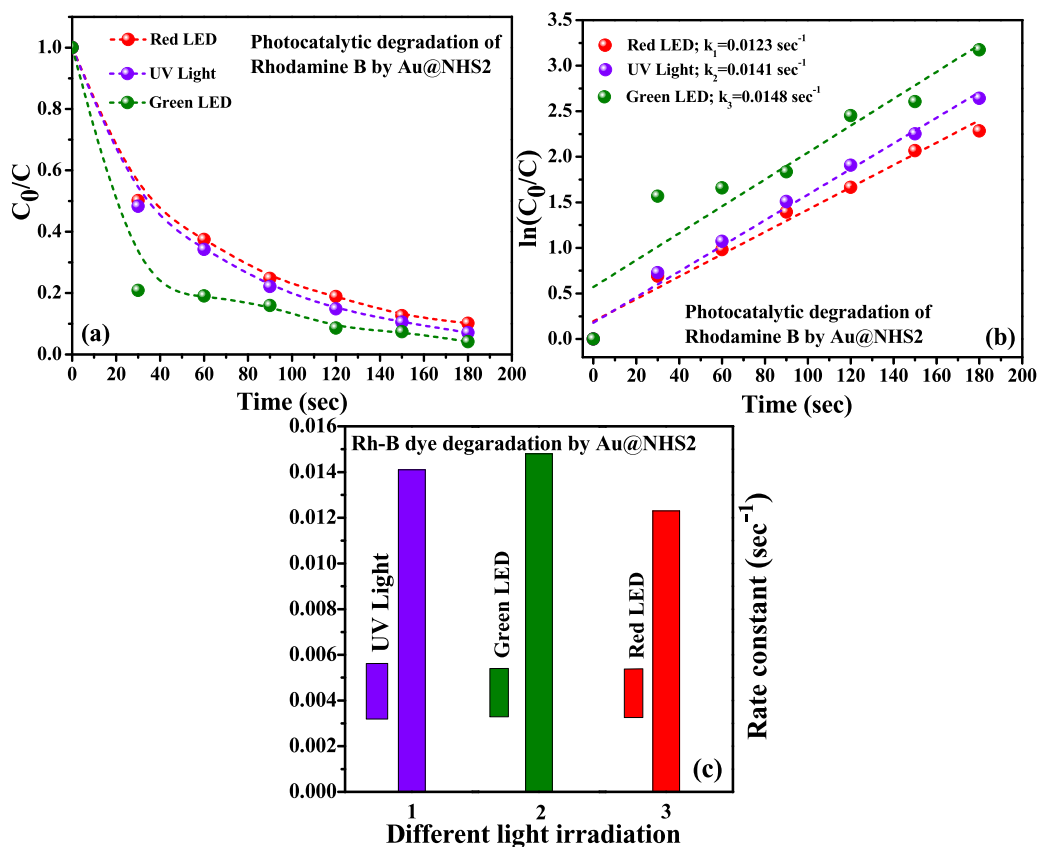
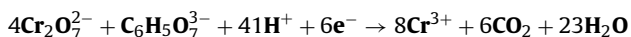


Fig. 10. (a)–(b) Photodegradation of Rh-B dye with UV and different LED lights. (c) Histogram plot of rate constant under different light irradiation.

Removal of toxic metal ions Cr(VI) from ground water is essential to get purified water. Reducing Cr(VI) to Cr(III), which is less toxic and easily precipitates under alkaline or neutral pH, is one of the promising ways to remove Cr(VI) toxicity from waste water. Citric acid has been used as hole scavenger. Fig. 8e and f shows the rate of Cr(VI) reduction in presence of different photocatalyst. Irradiation of Cr(VI) solution in presence of citric acid or in absence of any catalysis does not lead to any reduction of Cr(VI). Reduction kinetics has been monitored by absorbance spectroscopy with characteristic peak of Cr(VI) at 543 nm (SI, Fig. S8c). As-synthesized Bi_2S_3 nanourchin shows good photocatalytic reduction of Cr(VI) with a rate constant of $1.47 \times 10^{-2} \text{ min}^{-1}$. The maximum rate constant is achieved for Au@NHS2 heterostructure with a rate constant of 0.12 min^{-1} , which is nearly 10 times higher than pure Bi_2S_3 . The redox mechanism for conversion of Cr(VI) to Cr(III) can be expressed as follows:



Thus Cr contaminated wastewater can be purified by environmental friendly photocatalysis process.

The long term cycling stability is an essential requirement for its practical use in photocatalytic experiments. During the recycle experiments, Au@NHS2 were recollected and reused for five times for photocatalytic degradation shown in Fig. S11–S13 in supporting information. We have found that the rate constants (0.0247 s^{-1}) are same up to five cycles which proves that the as synthesized system is a robust catalyst. For better understanding the photocatalytic activity of ternary heterostructure, we have performed photocatalytic experiment by using mixture of NHS2 and Au@ Bi_2S_3 to compare its catalytic activity with $\text{Bi}_2\text{S}_3/\text{TiO}_2/\text{Au}$ ternary heterostructure. From Fig. S14 we have found that ternary

heterostructure has better rate constant (0.0247 s^{-1}) than that of the mixture of binary heterostructures (0.0225 s^{-1}) for RhB dye degradation. For the reduction of 4-paranitrophenol and detection of Cr(VI) we have similar results. Thus we can say that ternary heterostructure has better photocatalytic activity than that of the mixing of binary heterostructures.

8.3.1. Identifying the photoinduced electrons by ESR-spin label

Electron spin resonance (ESR) spectroscopy based on spin label TEMPO molecule is used to provide direct evidence of electron transfer under photoexcitation in Bi_2S_3 , Au@ Bi_2S_3 , NHS2 and Au@NHS2. The unpaired electrons in TEMPO molecule generate strong ESR signals as illustrated in Fig. 9a recorded in toluene solution at 77 K [53]. The photogenerated electrons in semiconductors can reduce TEMPO to ESR silent hydroxyl amine (TEMPOH) [54,55]. Thus systematic observation of ESR signal intensity under identical experimental conditions with the addition of photocatalysts can demonstrate the photoinduced electron transfer from semiconductor to TEMPO molecule. The ESR spectra at 77 K of TEMPO were collected in the presence of Bi_2S_3 , Au@ Bi_2S_3 , NHS2 and Au@NHS2 after 10 min of irradiation (Fig. 9b–e). The ESR spectra suggest that relative intensity of main peak at about 330 mT of TEMPO molecule is considerably damped with the addition of photocatalysts. Normally the free TEMPO radical does not react with oxidising species such as superoxide or holes and the systems before irradiation. Therefore damping of ESR signal is mainly associated with the generation of TEMPOH from TEMPO. The formation of TEMPOH clearly proves that electrons transfer from photoexcited semiconductor heterostructures to TEMPO molecule [56]. Moreover, ESR spectrum of Au@NHS2 is significantly damped indicating the best photocatalytic activity.

8.3.2. Beyond the maximum: plasmonic sensitization

As developed $\text{Bi}_2\text{S}_3/\text{TiO}_2/\text{Au}$ ternary NHS shows excellent photocatalytic activity, the role of plasmonic absorbance of gold nanoparticles has been studied for better understanding and maximisation of photoactivity. For this purpose, wavelength dependent catalytic activity has been studied with UV and LED lamps irradiation including green (550 nm) and red (700 nm) with same irradiance intensity (optimised by a photometer). According to Fig. 10, maximum photocatalytic activity (RhB degradation) has been found with green LED excitation. As the plasmonic absorbance of Au nanocrystals (NCs) is in the green region of visible light so we can expect plasmon induced visible light activity of the material. For small spherical metal NCs where the far-field and near-field resonant frequency overlap completely, the highest near-field enhancement can be achieved when light is resonant with the Au NCs LSPR as they act as the concentrator of the local electric field. The optical absorbance mechanism of a semiconductor is described by Fermi's golden rule in electric dipole approximation. In semiconductor, the absorbance increases linearly with the intensity of the perturbation electric field. The near field enhancement can significantly enhance the inter-band or other optical transitions in the nearby semiconductor if the LSPR spectra overlap with them [57,58]. Absorbance spectra of Au@NHS2 show a significant overlap of Au plasmonic absorbance and Bi_2S_3 band gap absorbance. The enhancement of light absorbance can be estimated using the following equation [59]:

$$\text{FE} = \frac{\int_V dZ \int dx dy |E(x, y, z)|^2}{\int_V dZ \int dx dy |E_0|^2}$$

Where the integrating volume (V) refers to the volume in the semiconductor covered by the near-field. $E(x, y, z)$ is the value of the near-field at point (x, y, z), and E_0 is the electric field of incident light. As the maximum area of Bi_2S_3 nanorods are covered with Au NCs, V value is expected to be high. Thus the light absorption efficiency and also the rate of generation of e-h pair increases due to energy transfer through the near field enhancement. But we cannot conclude at this state, whether the direct electron transition from Bi_2S_3 to Au or electric field enhancement due to plasmonic absorbance of Au plays the crucial role for high photoactivity.

For most plasmonic photocatalysis, metal nanoparticles serve as a sensitizer by greater utilization of the solar spectrum. By tailoring the size of the metal particles one can trigger the plasmon absorption from the visible to NIR region. Not only size but also the geometry affects the LSPR frequency as the asymmetry enables the electrons to resonate in more than one mode. Now to investigate the effect of near field enhancement we change the size and geometry of the Au nanoparticles. First of all we fabricate a 2-D array of Au NCs (~10 nm, SI, Fig. S16a) deposited over glass slide and a thin layer of non-conducting tetra-ethyl orthosilicate (TEOS) layer (5 nm) was deposited over Au NCs. NHS2 was deposited over TEOS to develop a sandwich device where direct transfer of carrier is not possible from metal to semiconductor or vice-versa. The device shows absorbance centered at 570 nm for Au LSPR absorbance (SI, Fig. S15a). Wavelength dependent photocatalytic activity study shows maximum activity can be obtained with green LED excitation shown in the SI, Fig. S17. Direct excitation of TiO_2 (with UV light) and Bi_2S_3 leads to poor catalytic activity. Here direct charge transfer between Au and Bi_2S_3 is not possible as there is an insulating layer between them. The near field enhancement is solely responsible for greater photoactivity as excitation with green LED leads to direct excitation of Au nanoparticles. Another device has been developed in similar way with Au nanorods (TEM in SI, Fig. S16b). Where LSPR absorbance for longitudinal mode is found at 653 nm (SI, Fig. S15b) which is coupled with absorption spectra of

Bi_2S_3 . Excitation with red LED (700 nm) thus gives the maximum photoactivity (SI, Fig. S18).

So, from above experiments we can conclude that direct plasmonic excitation of Au NPs maximise the photoactivity of $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructure. The photoactivity of Au@NHS2 under the solar irradiance ($k = 0.025 \text{ s}^{-1}$) was found to be higher than with green LED excitation ($k = 0.014 \text{ s}^{-1}$). Under solar irradiance simultaneous excitation of TiO_2 , Bi_2S_3 and Au plasmonic is possible. The metal nanoparticles absorb, intensify and direct the light to the semiconductors for more absorption and also enhance e-h pair formation by near field enhancement. Also we have successfully fabricated a visible light photocatalytic device to convert visible light energy to chemical energy with a 2D array of Au NPs or NRs as a near field enhancing layer. So we can conclude that not only heterostructure formation but also plasmon induced near field enhancement is potential for photocatalytic performance.

9. Conclusion

In summary, we have successfully synthesized high quality $\text{Bi}_2\text{S}_3/\text{TiO}_2/\text{Au}$ nanoscale heterostructure, in which both TiO_2 and Au NCs are epitaxially grown on the surface of Bi_2S_3 nanorods. We found that oleic acid plays a crucial role for the formation of nanorod assembly of Bi_2S_3 urchin morphology. Epitaxial interface of semiconductor-semiconductor and semiconductor-metal and proper band alignment of individual component favor the separation of electron-hole pair. The best photocatalytic activity is achieved for a particular Bi: Ti ratio i.e. 1:1.33. Absorption of light over a wide wavelength region, transportation of photo generated electrons and holes and creation of high near field through the plasmonic excitation improve the photocatalytic degradation of RhB, reduction of 4-nitrophenol and removal of Cr(VI) from water. Solid state device consisting of low and high band gap semiconductors and plasmonic metals can be used for efficient and eco friendly removal of pollutants in wastewater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.07.057>.

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